

Rheological Properties of Dispersions of Spherulites from Jet-Cooked High-Amylose Corn Starch and Fatty Acids

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ABSTRACT

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High-amylose corn starch was cooked in an excess-steam jet cooker in the presence of 5% oleic or palmitic acid, based on amylose. The cooked product was rapidly cooled in an ice bath and then freeze-dried or drum-dried. Amylose was removed from solution by forming helical inclusion complexes with the fatty acid, and the inclusion complexes formed sub-micron spherical particles upon cooling. The dried material was reconstituted to form a paste that exhibited gel-like properties upon standing,

but that flowed readily when shear was applied. The rheological properties of these pastes were measured to determine the effects on the flow properties of 1) the solids concentration in the reconstituted paste, 2) the method of sample drying and reconstitution, and 3) the fatty acid used. The materials were very spreadable, and at the highest concentrations their flow properties were similar to a commercial shortening. The pasting properties of the dried solids were also examined.

Steam jet cooking is a rapid and continuous process that is widely used to prepare aqueous dispersions of starch for commercial applications (Klem and Brogley 1981). Excess-steam jet cooking is currently being studied as a convenient and inexpensive processing method for preparing new starch-based compositions. When dilute starch dispersions are jet-cooked and cooled, spherulites can form from the crystallization of helical inclusion complexes that form from amylose and the native lipids normally present in cereal starch granules. Two different types of spherulites were observed when corn starch was jet-cooked and slowly cooled (Fanta et al 2002). Both small, toroidal, and larger, more spherical particles were formed, and the two spherulite species had different crystalline structures. Spherulite morphology has also been shown to depend on the cooling rate, the presence of oil, and fatty acid structure (Fanta et al 2005; 2006).

In an effort to obtain high yields of the spherulites to develop end-use applications, Fanta et al (2008) jet-cooked high-amylose corn starch and added sufficient pure fatty acid to complex all of the available amylose. Yields of spherulites $\leq 63\%$ based on total starch content were obtained. The previously observed toroidal and spherical particles were again observed for slowly cooled samples, with their relative proportions depending on the amount of added fatty acid and the stirring conditions during cooling. However, when the jet-cooked dispersions were rapidly cooled in an ice bath, the toroidal and spherical morphologies were not observed. Instead, the particles formed consisted entirely of sub-micron spherical particles and aggregates of these particles. In this report, we describe the rheological properties of aqueous pastes formed from these particles.

The effects of amylose inclusion complexes on the rheology of starch gels have been previously studied in a number of systems (Eliasson 1988; Eliasson et al 1988; Biliaderis and Tonogai 1991; Conde-Petit and Escher 1995). Gelatinized starch samples were used in these studies, and the inclusion complexes increased gel strength by enhancing interactions between swollen starch granules. In contrast, the corn starch used in this study was completely

solubilized under the high temperature and shear conditions of the jet cooker.

MATERIALS AND METHODS

Materials

High-amylose corn starch (AmyloGel 03003, containing $\approx 70\%$ amylose) was a product of Cerestar, Hammond, IN. Percent moisture was calculated from weight loss after drying at 100°C under vacuum, and all weights of starch are given on a dry weight basis. Oleic acid (NF/FCC) was purchased from Fischer Scientific (Fair Lawn, NJ). Palmitic acid ($\approx 99\%$) was from Sigma Chemical (St. Louis, MO). The vegetable shortening used for comparison of rheological properties was Crisco (J. M. Smucker, Orrville, OH).

Jet Cooking Starch/Fatty Acid Mixtures and Isolation of Crystallites

In a typical experiment, 4.20 g of oleic acid (5%, by weight, based on amylose, assuming 70% amylose in the starch sample) was intimately mixed with 120.0 g of high-amylose corn starch. For experiments with palmitic acid, palmitic acid was dissolved in ≈ 20 mL of ethanol and the solution was mixed with the starch. The ethanol was then allowed to evaporate under ambient conditions. The starch/fatty acid mixture was dispersed in 1,200 mL of water and the dispersion was passed through a laboratory model steam jet cooker (Penford, Cedar Rapids, IA), operating under excess steam conditions (Klem and Brogley, 1981). Temperature in the hydroheater was 140°C , the steam back pressure was 40 psig (380 kPa) and the steam line pressure from the boiler was 65 psig (550 kPa). Pumping rate of the aqueous starch dispersion through the jet cooker was ≈ 1 L/min. Jet-cooked dispersion (≈ 900 mL) was collected in a 1-L stainless steel Dewar flask (series 3763, Cole-Parmer Instrument, Vernon Hills, IL). Before collecting the sample, the Dewar flask was heated with hot (100°C) water from the jet cooker.

Percent solids in jet-cooked dispersions, determined by freeze-drying weighed portions of dispersion, were 4.0–4.3%. Variations in %solids were caused by dilution of cooked dispersions with varying amounts of condensed steam. Dispersions were rapidly cooled by pouring into a 2-L beaker and cooling to $\approx 25^\circ\text{C}$ in an ice water bath, while gently stirring with a spatula. Cooling times were 7–12 min. Materials were dried on a double-drum drier (model 20, Drum Drier and Flaker, South Bend, IN) heated with steam at 310 kPa (135°C). The flake-like product was ground to a coarse powder in Retsch mill (type ZM1, Brinkmann Instruments, Westbury, NY).

Spherulites were isolated by diluting cooled dispersions with water to give a 10-fold reduction in solids concentration and centrifuging (GS-6KR, Beckman Coulter, Fullerton, CA) at 3,000 rpm

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($\approx 2000 \times g$). Dissolved starch was removed from the precipitated spherulites by washing three times with excess water followed by centrifugation. Percent yield was determined by freeze-drying the water-washed spherulites isolated from a weighed portion of jet-cooked dispersion. The amylose content of the supernatant was determined by measuring the absorbance of the amylose-iodine complex in a 90% DMSO solution (Knutson 1986).

Redispersion and Flow Property Measurements

Drum-dried samples were redispersed by heating for 30 min in a water bath at 95°C with gentle shaking, followed by 5 min of mixing with an Ultra-Turrax T25 disperser (Janke & Kunkel, Staufen, Germany) with a 1-mm mixing head at 13,500 rpm. Freeze-dried samples were mixed by hand with a spatula with no additional heating.

Measurements in small amplitude oscillatory shear flow were conducted on a controlled strain fluids rheometer (ARES, TA Instruments, New Castle, DE). Tests were performed with a 50-mm diameter cone-and-plate geometry at a strain of 1%, which was within the linear viscoelastic region for all samples. A circulating water bath was used to maintain the temperature at $25.0 \pm 0.1^\circ\text{C}$, and humidity covers were used to prevent drying the samples. All measures were done in duplicate and average values are reported.

The spreadability of the materials was measured at room temperature with a texture analyzer (TA.XTPlus, Stable Micro Systems, Godalming, Surrey, UK). Samples were loaded into a female 90° cone and a matched male cone was lowered into the sample at 3 mm/sec and then retracted at 10 mm/sec. The yield stress was measured with a controlled stress rheometer (AR2000, TA Instruments, New Castle, DE) using 40-mm diameter cross-hatched steel plates. A continuously increasing stress of 0.01–100 Pa was applied to the sample until it began to flow. The pasting cell of the controlled stress rheometer was used to measure the apparent viscosity of the samples at 60 rpm. The pasting cell consists of a 36.9-mm diameter cylinder and an impeller (32.5 mm o.d., 12.5 mm, high). The samples (30 mL) were heated from 25 to 95°C at 4°C/min, held at 95°C for 10 min, and cooled to 25°C at 4°C/min.

Microscopy

Cooled dispersions were examined by placing a drop of sample on a microscope slide and gently overlaying with a cover slip to minimize pressure and shear. Images were photographed using a Zeiss Axioskop light microscope (Carl Zeiss, Thornwood, NY) and representative fields were photographed using a digital camera (D70s, Nikon, Tokyo, Japan) using phase contrast optics.

Differential Scanning Calorimetry

Samples of the isolated spherulites were analyzed using a differential scanning calorimeter (Q2000 MDSC, TA Instruments,

New Castle, DE). Samples (23 mg) were sealed in stainless steel DSC pans and heated from 10 to 250°C at a heating rate of 10°C/min.

RESULTS AND DISCUSSION

Previous work (Fanta et al 2008) has shown that when high-amylose corn starch and fatty acids are steam-jet-cooked together, a variety of spherulite morphologies were obtained depending on the cooling conditions. This study considers only jet-cooked dispersions that were rapidly cooled in an ice bath while being stirred gently. Under these conditions, high yields ($\approx 62\%$ based on the total starch content) of submicron spherical particles were obtained. Scanning electron and light microscopy showed that micron-sized aggregates of these particles were also formed and X-ray diffraction showed that the crystallites had a 6_1V conformation.

The amylose/fatty acid spherulites can be isolated from dissolved amylopectin by dilution and centrifugation, and can be obtained at concentrations of ≈ 16 wt%. The resulting product is a smooth paste that flows readily when deformed and has a gel-like appearance. Pastes prepared by this method are smooth to the touch, with no apparent grittiness or stickiness, and feel qualitatively similar to the texture of a semi-solid shortening. A photomicrograph of the spherulites is shown in Fig. 1. The individual spherulites cannot be observed at this resolution but the micron-sized aggregates can be seen. The aggregates are sufficiently concentrated that they can form a network throughout much of the sample and lead to the gel-like properties.

Linear viscoelastic properties of an amylose/oleic acid spherulite paste at 16% solids are shown in Fig. 2. The storage modulus (G') and the loss modulus (G'') remain nearly independent of the measurement frequency (ω) and $G' > G''$ at all frequencies. This behavior is characteristic of a gel and is consistent with the material's paste-like appearance. The linear viscoelastic properties are also shown for the spherulite dispersion when diluted to 10 wt%. Although the qualitative behavior is the same as for the sample at 16 wt%, the values of the moduli drop by over two orders of magnitude for this dilution. Because the network shown in Fig. 1 suggests contact between aggregates rather than intermolecular bonding or interparticle attraction, dilution has an es-

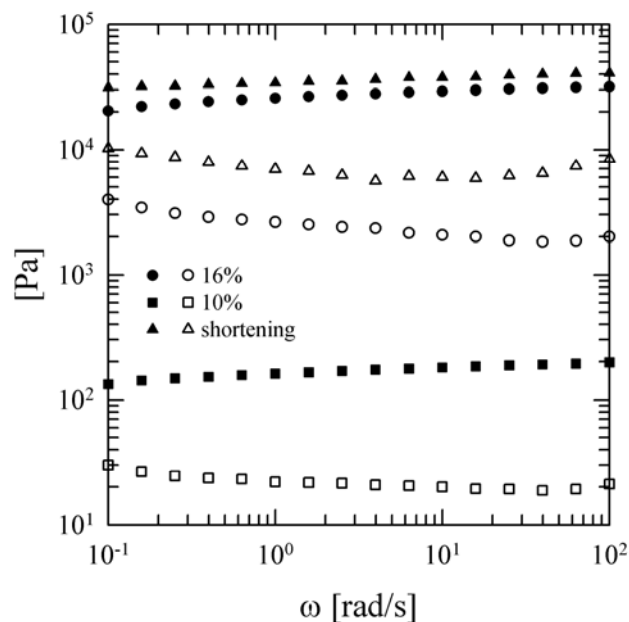


Fig. 2. Linear viscoelastic properties of amylose/oleic acid spherulites at 10 and 16 wt%. Also shown are properties of commercial shortening. Storage modulus (G') is shown by solid symbols and loss modulus (G'') is shown by open symbols.

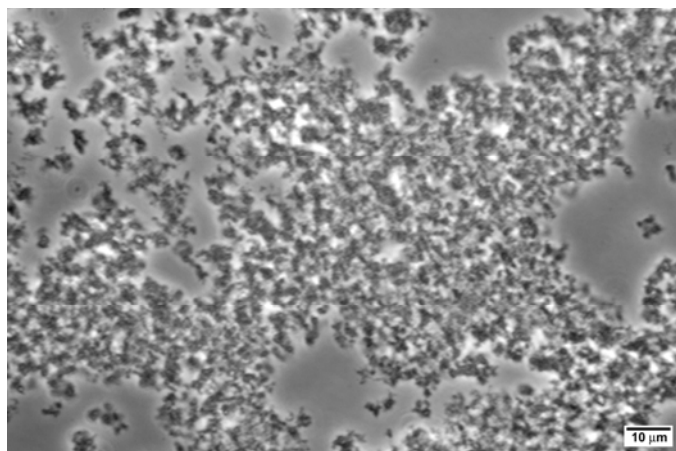


Fig. 1. Amylose/oleic acid spherulites isolated by centrifugation.

pecially strong effect on the rheological properties. Figure 2 also shows the linear viscoelastic properties of a commercial vegetable shortening. The loss modulus of the shortening is higher than that of the 16 wt% spherulite sample but the range of modulus values confirms the qualitative observation of their similarity.

To develop materials for larger scale applications, it is desirable to avoid the large volume dilution and centrifugation required to isolate spherulites from the remaining dissolved starch. Because the gel-like properties discussed above are not observed in jet-cooked dispersions prepared at the low concentrations used in this study, we examine the properties of materials that were drum-dried and then reconstituted at higher concentrations. The dried materials offer the further advantages of ease of storage and

handling. The most complete redispersion of the drum-dried samples (as indicated by higher modulus values) was obtained by heating the materials in a water bath at 95°C for 30 min, followed by 5 min of mixing with a high-shear dispersing mixer. Longer mixing periods did not further increase the modulus values, and eventually the modulus values decreased with additional mixing, presumably due to mechanical degradation of the dissolved starch. Although the heating was intended to redisperse the amorphous starch surrounding the spherulites, the effect of heating on the spherulites must also be considered. The thermal stability of amylose-lipid complexes has been studied by differential scanning calorimetry (Stute and Konieczny-Janda 1983). The peak temperature for dissociation was 103°C for palmitic acid and ≈98°C for oleic acid. Both peaks covered a broad temperature range, so some dissociation would be expected at 95°C. However, the high yield of starch in the spherulites (≈62%) suggests that few inclusion complexes remain in solution. Differential scanning calorimetry measurements of the isolated spherulites showed a melting transition at 195°C (data not shown), so the reconstitution method should not have any effect on the spherulites.

The linear viscoelastic properties of the reconstituted drum-dried starch/oleic acid materials at 10 and 15 wt% are shown in Fig. 3. Both reconstituted materials showed the same gel-like behavior as was seen for the isolated spherulites. The 15 wt% sample had modulus values similar to the 16 wt% spherulite sample and the commercial shortening. However, this sample only contains ≈9.3 wt% spherulites, the remaining material being uncomplexed amylopectin. The additional starch in solution provides a higher solvent viscosity than water for the spherulites. The higher solvent viscosity also results in a decreased concentration dependence of the modulus values. The 10 wt% sample (6.2% spherulites) had modulus values only about a factor of 10 lower than the 15 wt% sample, in contrast to the 100-fold decrease in values for isolated spherulites shown in Fig. 2. Amylose content measurements of the starch that did not form spherulites showed that ≈90% of the amylose was complexed for materials prepared with 5% oleic acid. Fanta et al (2008) showed that when palmitic acid was used, the spherulite yield increased for palmitic acid concentrations ≤5% and then decreased slightly for 10% palmitic acid. Furthermore, experiments with drum-dried and reconstituted materials prepared

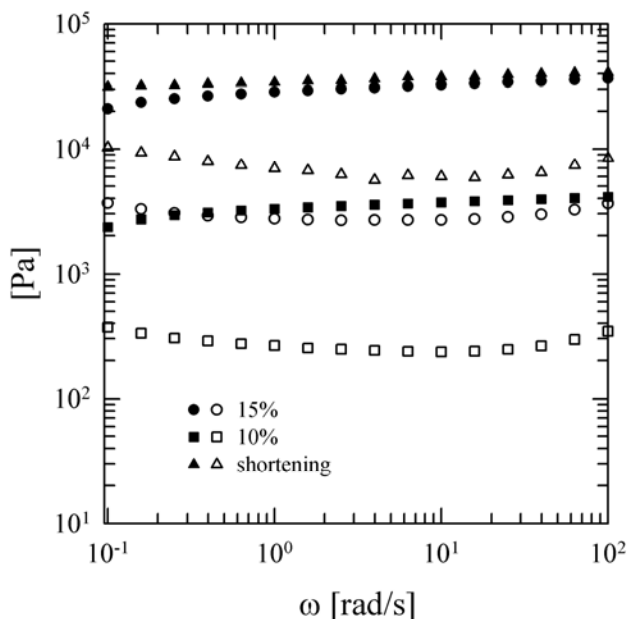


Fig. 3. Linear viscoelastic properties of reconstituted drum-dried starch/oleic acid materials at 10 and 15 wt%. Also shown are properties of commercial shortening. Storage modulus (G') is shown by solid symbols and loss modulus (G'') is shown by open symbols.

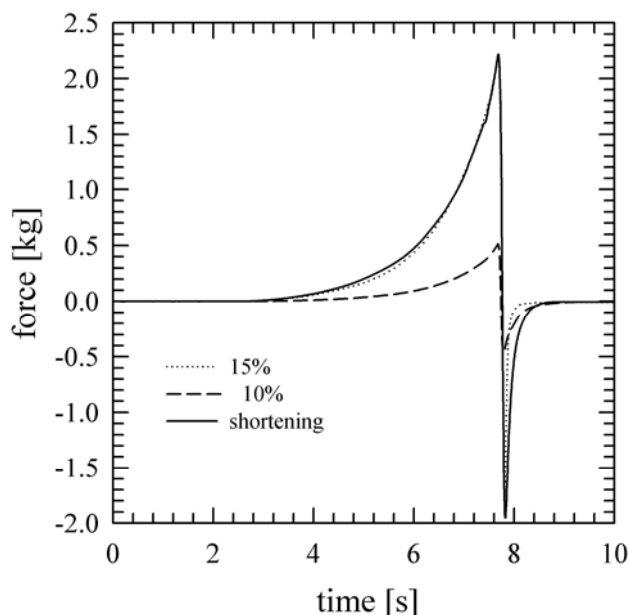


Fig. 4. Spreadability test in a texture analyzer. Upper cone moved down at 3 mm/sec and up at 10 mm/sec.

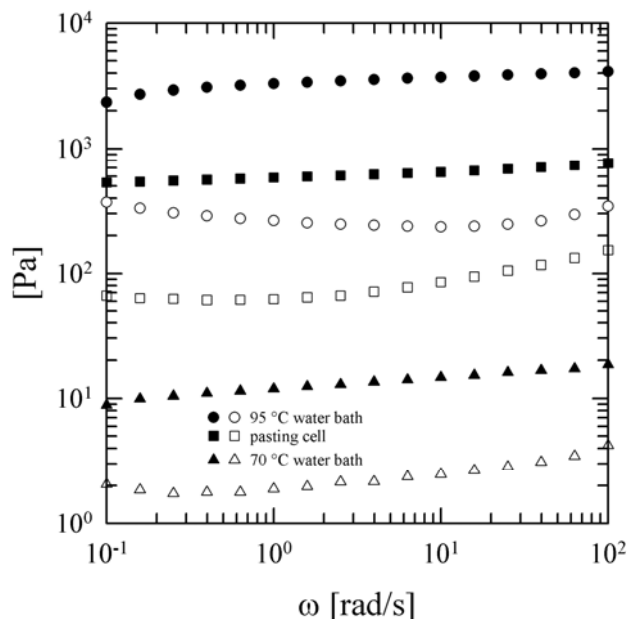


Fig. 5. Linear viscoelastic properties of drum-dried starch/oleic acid materials at 10 wt% reconstituted by various methods. Storage modulus (G') is shown by solid symbols and loss modulus (G'') is shown by open symbols.

with 10% oleic acid had modulus values only $\approx 10\%$ higher than the materials prepared with 5% oleic acid (data not shown).

Measurements of the modulus values provide information about the structure of the sample through small amplitude deformations but they cannot characterize the material under flow conditions. Typically the viscosity would be measured as a function of shear rate to characterize the flow properties of a material. However, standard viscosity measurements were not suitable for these materials due to slip of the sample in the rheometer. Instead, the materials were compared with the commercial shortening using the spreadability test in a texture analyzer. The low resistance to deformation is shown in Fig. 4, where the upper cone has penetrated ≈ 10 mm into the sample before the measured force begins to increase. In contrast, a rigid gel would be expected to have a larger initial force measurement. As the upper cone continues to travel downward, the sample is squeezed out of the bottom cone and the measured force increases sharply. Despite the complex flow created in this test, the 15 wt% solids sample displayed a deformation curve nearly identical to the commercial shortening. The 10% solids sample shows a similar qualitative response. The major difference between the samples can be seen at $t > 7.67$ sec when the upper cone is retracted. The negative force indicates a resistance to raising the cone and the more rapid decrease in its magnitude for the starch samples indicates that the materials are less sticky than the shortening. The spreadability can be compared with a range of other materials by measuring the yield stress and yield strain. Daubert et al (1998) showed that a combination of these measurements could be used to classify the spreadability of food products. The yield stress for the material was 52 Pa at a strain of 0.5. These values fall in the range of “easy” spreadability and were similar to those of nonfat sour cream and fat-free yogurt.

The effect of the reconstitution method of drum-dried samples on the linear viscoelastic properties is shown in Fig. 5. The results

for samples heated to 95°C for 30 min and then mixed with the dispersing mixer for 5 min are included for comparison. Also shown are results for a sample heated to 70°C for 30 min and mixed with the dispersing mixer and results for a sample reconstituted in the pasting cell. The sample heated to 70°C did not form a smooth paste similar to the other samples previously discussed. Instead, it consisted of nonhomogenous wetted flakes of drum-dried material and a large amount of free water. The differences between samples can be seen in the photomicrographs in Fig. 6. When the cooled material was drum-dried and milled, it formed flakes that did not easily redisperse in water. Figure 6A shows drum-dried material after being added to room temperature water and mixed by hand. The majority of the starch remained as large flakes and only a few small aggregates of spherulites were observed. After heating at 70°C for 30 min and mixing with the dispersing mixer for 5 min, more spherulites and spherulite aggregates were present (Fig. 6B). However, even though the drum-dried flakes appear to have been rounded by the mixing procedure, neither shearing nor heating caused the flakes to be well dispersed and the sample remained nonhomogenous. Figure 6C shows the drum-dried flakes after heating to 95°C for 30 min and shearing with the dispersing mixer for 5 mins. Under these conditions, the flakes were completely broken up and the aggregates of spherulites again form a network throughout the sample.

The importance of heating on redispersing drum-dried spherulites was examined by heating the materials in the pasting cell while stirring at 60 rpm. The viscosity is a function of time in Fig. 7 for drum-dried and freeze-dried samples containing both the spherulites and amylopectin, as well as for spherulites that had been freeze-dried. The viscosity of the drum-dried sample was initially high due to nonuniform dispersion but decreased with increasing temperature. The viscosity increased as the temperature rose $>85^\circ\text{C}$. Because samples were jet-cooked, this increase is not due to starch gelatinization but may be due to increased

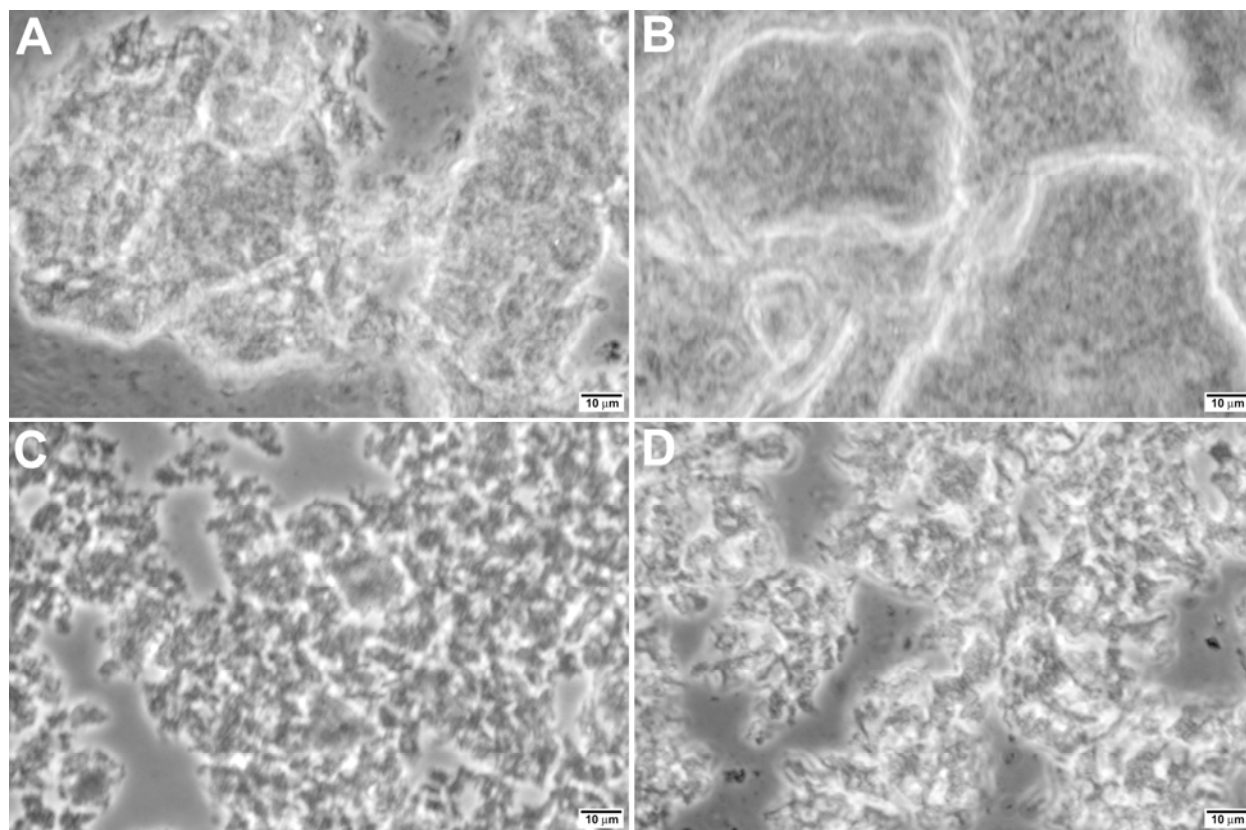


Fig. 6. Photomicrographs of reconstituted starch/oleic acid materials. **A**, Drum-dried material stirred by hand; **B**, drum-dried material heated to 70°C and stirred with a dispersing mixer; **C**, drum-dried material heated to 95°C and stirred with a dispersing mixer; **D**, freeze-dried material stirred by hand.

swelling and solubility of uncomplexed amylopectin when the temperature was increased. The linear viscoelastic properties of the drum-dried sample after heating in the pasting cell are shown in Fig. 5 along with the linear viscoelastic properties observed with the other reconstitution methods. Although the moduli were higher than those of the sample that was only heated to 70°C, they were lower than those of the sample heated to 95°C. The rapid rise of the viscosity in the pasting cell suggests that the amount of time at 95°C is not the most important factor in the dispersion of drum-dried flakes. Rather, the relatively mild mixing in the pasting cell was not sufficient to disperse the flakes in comparison to high shear mixing in the dispersing mixer.

Cooled starch/oleic acid samples were also freeze-dried and when these samples were added to water, they readily dispersed with hand mixing to form smooth pastes. Freeze-dried material shown in Fig. 6D consisted of domains of spherulite aggregates

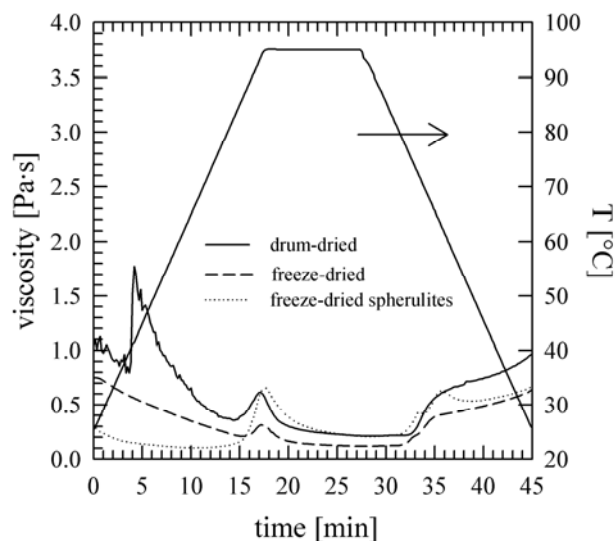


Fig. 7. Viscosity of isolated amylose/oleic acid spherulites and drum-dried and freeze-dried starch/oleic acid materials during heating and cooling in the pasting cell.

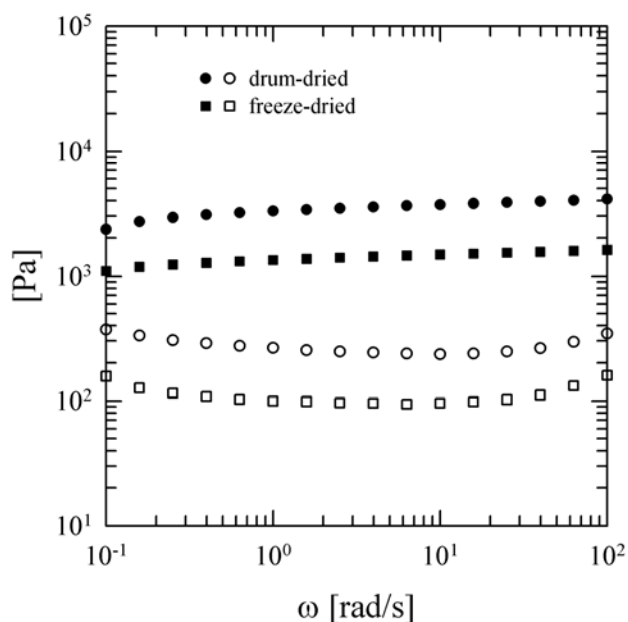


Fig. 8. Linear viscoelastic properties of drum-dried and freeze-dried starch/oleic acid materials at 10 wt%. Storage modulus (G') is shown by solid symbols and loss modulus (G'') is shown by open symbols.

bound together by the remaining uncomplexed amylopectin. Although the aggregates are not as small as those observed in the heated and sheared samples, the freeze-dried samples had the same appearance and feel of smooth pastes. The linear viscoelastic properties of Fig. 8 show that the freeze-dried material had slightly lower modulus values than the drum-dried material. However, given the ease of redispersing these samples, they may be preferable to the drum-dried materials for some applications.

Samples were also prepared using palmitic acid in place of oleic acid. As shown previously (Fanta et al 2008), spherulites with similar morphology were formed in similar yields for both fatty acids. When redispersed, palmitic acid samples also formed the same smooth pastes. However, Fig. 9 shows that the linear viscoelastic properties of the samples formed with palmitic acid were lower than those of the samples formed with oleic acid. The storage modulus values for the 15% palmitic acid sample were nearly equal to the values of the 10% oleic acid sample. The same trend was also observed in the spreadability test in the texture analyzer (data not shown). Because the spherulite concentration is the same for each case at a given solids concentration, differences in the solvent viscosity could account for the observed differences. The extent of redispersion is important in determining the rheological properties of the materials so drum-dried flakes of materials prepared with oleic acid may be more easily dispersed. The lower melting point of oleic acid may also cause the breakdown of complexes at a lower temperature than for palmitic acid.

CONCLUSIONS

Smooth pastes can be formed from dispersions of the spherulites that result from rapidly cooling jet-cooked mixtures of high-amylose corn starch and fatty acids. The spherulites are submicron spherical particles that form aggregates, and the aggregates form a network throughout the sample. The pastes can be prepared from either isolated, undried spherulites or from dried and reconstituted material containing uncomplexed amylopectin. A wide range of material properties can be obtained, depending on the concentration of material, the drying and reconstitution method, and the fatty acid used to form the spherulites. At the highest concentrations, the flow properties of the materials are

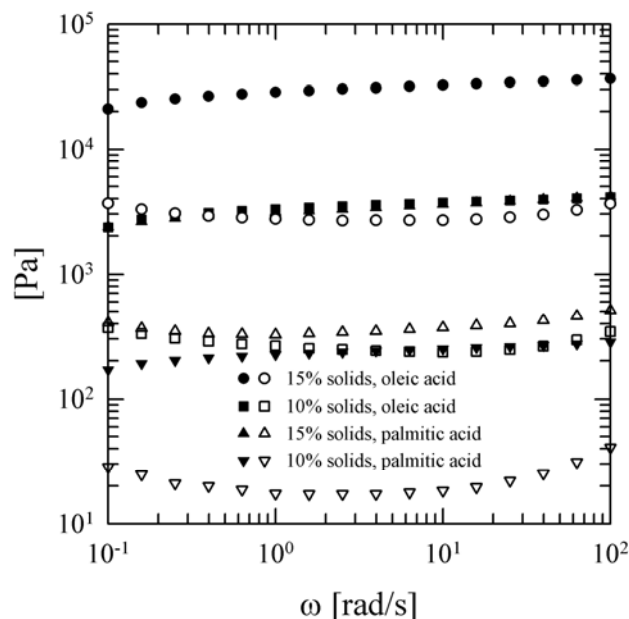


Fig. 9. Linear viscoelastic properties of drum-dried materials formed with oleic acid and palmitic acid at 10 and 15 wt%. Storage modulus (G') is shown by solid symbols and loss modulus (G'') is shown by open symbols.

similar to those of a commercial shortening. The variety of materials with desirable flow properties that can be formed make this system suitable for a range of end-use applications.

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